This assignment is due at the beginning of class on Wednesday, September 24th.

1. For two electrons (1 and 2) with the same spin (both $\alpha$ or both $\beta$) in the same atom we can write $\psi_{\text{spin}} = \alpha(1)\alpha(2)$ or $\psi_{\text{spin}} = \beta(1)\beta(2)$. But for two electrons with opposite spins in the same atom we cannot write $\psi_{\text{spin}} = \alpha(1)\beta(2)$ or $\psi_{\text{spin}} = \alpha(2)\beta(1)$. Instead, we must write either $\psi_{\text{spin}} = [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$ or $\psi_{\text{spin}} = [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$. Why?

   A function like $\psi_{\text{spin}} = \alpha(1)\alpha(2)$ or $\psi_{\text{spin}} = \beta(1)\beta(2)$ is allowable because it does not differentiate between two indistinguishable electrons. But $\psi_{\text{spin}} = \alpha(1)\beta(2)$ or $\psi_{\text{spin}} = \alpha(2)\beta(1)$ says that a specific electron has a specific spin state. We cannot know that, because the electrons are indistinguishable.

2. The following are wave functions for two electrons in an atom. All have the form $\psi = \psi_{\text{orbital}}\psi_{\text{spin}}$, where 1 and 2 indicate the individual electrons and $\alpha$ and $\beta$ indicate the two spin states. Indicate any function that is allowed and any that is disallowed by the Pauli Principle. Show the basis of your decision in each case by writing the wave function as transformed by electron exchange. Explain in words what the wave function is describing; e.g., $\psi = [1s(1)1s(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$ means “two electrons in 1s orbitals with opposite spins”.

   $\psi = [1s(1)2s(2) - 1s(2)2s(1)][\alpha(1)\alpha(2)]$
   $\psi = [1s(1)1s(2)][\alpha(1)\beta(2) + \alpha(2)\beta(1)]$
   $\psi = [2s(1)2s(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

   $\psi = [1s(1)2s(2) - 1s(2)2s(1)][\alpha(1)\alpha(2)] - \psi = [1s(2)2s(1) - 1s(1)2s(2)][\alpha(2)\alpha(1)]$

   The $\psi_{\text{orbital}}$ part is antisymmetric, because it changes sign with electron exchange. The $\psi_{\text{spin}}$ part is symmetric, because exchange gives an equivalent expression with the same sign. The product of the two parts is antisymmetric and therefore allowed by the Pauli principle. The wave function describes two electrons with the same spin in separate orbitals (1s and 2s).

   $\psi = [1s(1)1s(2)][\alpha(1)\beta(2) + \alpha(2)\beta(1)] - \psi = [1s(2)1s(1)][\alpha(2)\beta(1) + \alpha(1)\beta(2)]$

   Interchange of electrons leads to the same expression, simply written in different order. The sign of the overall function is the same and therefore symmetric. This is not allowable by the Pauli principle for electrons. The wave function describes two electrons in the same orbital with opposite spins. However, the specific spin function is symmetric and leads to an overall symmetric function. The allowable spin function would be $\psi_{\text{spin}} = \alpha(2)\beta(1) - \alpha(1)\beta(2)$, which is antisymmetric and would make the overall function antisymmetric.
\[ \psi = [2s(1)2s(2)](\alpha(1)\beta(2) - \alpha(2)\beta(1)) \quad \psi = [2s(2)2s(1)](\alpha(2)\beta(1) - \alpha(1)\beta(2)) \]

The orbital function is symmetric and the spin function is antisymmetric. Therefore, interchange of electrons leads to an expression with the opposite sign, owing to the antisymmetric spin function. Like the preceding function, this describes two electrons with opposite spins in the same orbital (here, 2s), but this time the spin function is antisymmetric and therefore allowable by the Pauli principle.

3. The bond dissociation enthalpies for the N–N bond in \( \text{N}_2 \) and \( \text{N}_2^- \) are 945 and 765 kJ/mol, respectively. Give the MO electronic configuration for each species [using the notation \((\sigma_2s)^2(\sigma^*_2s)^2 \ldots \)], and account for the difference in bond strength.

\[
\begin{align*}
\text{N}_2 & \quad (\sigma_2s)^2(\sigma^*_2s)^2(\pi_2p)^4(\sigma_2p)^2 \\
\text{N}_2^- & \quad (\sigma_2s)^2(\sigma^*_2s)^2(\pi_2p)^4(\pi^*_2p)^1
\end{align*}
\]

The extra electron in \( \text{N}_2^- \) is added to an antibonding MO and therefore weakens the bond.

4. Sketch VB representations of the bonding in \( \text{B}_2 \) and \( \text{C}_2 \) to show which atomic orbitals are presumably overlapping to form the bonds. On the basis of these models, what are the bond orders? \( \text{B}_2 \) is paramagnetic and \( \text{C}_2 \) is diamagnetic. Do these observations agree with the VB models? Are the bond orders and observed magnetic properties correctly predicted by the MO models for \( \text{B}_2 \) and \( \text{C}_2^- \)? Explain.

\( \text{B}_2 \) VB model: a single bond formed by overlap of \( 2p \) orbitals

\( \text{C}_2 \) VB model: a double bond formed by \( 2p \sigma \) overlap and \( 2p \pi \) overlap.

Both VB models assume equal numbers of \( \alpha \) and \( \beta \) electrons (electron pairing) for both \( \text{B}_2 \) and \( \text{C}_2 \), thereby predicting that both will be diamagnetic. The MO models are

\[
\begin{align*}
\text{B}_2 & \quad (\sigma_2s)^2(\sigma^*_2s)^2(\pi_2p)^2 \\
\text{C}_2 & \quad (\sigma_2s)^2(\sigma^*_2s)^2(\pi_2p)^4
\end{align*}
\]

The MO model correctly predicts the magnetic properties. In \( \text{B}_2 \) the two electrons of \((\pi_2p)^2\) are in separate orbitals with the same spin, making \( \text{B}_2 \) paramagnetic. In \( \text{C}_2^- \), \((\pi_2p)^4\) has equal numbers of electrons with opposite spins and so is diamagnetic. In both cases, the bonding orbitals are \( \pi \) MOs, in contrast to the VB presumption that there must always be a \( \sigma \) bond at minimum.
5. The cyclobutadiene dianion, $C_4H_4^{2-}$, has six electrons in a delocalized $\pi$ system. Using the so-called “polygon rule” sketch the $\pi$-MO scheme, showing $\pi$-bonding, $\pi^\text{\text{non}}$-nonbonding, and $\pi^*$-antibonding levels. Show the filling of electrons in this scheme. What is the C–C bond order in $C_4H_4^{2-}$ (including both $\sigma$ and $\pi$ contributions)? Account for the fact that $C_4H_4^{2-}$ is much less stable than benzene.

The so-called “polygon rule” is based on the general result that the ordering of $\pi$ MOs for planar delocalized $\pi$ systems is laid out like the carbon ring itself, with the point of the figure down. For $C_4H_4^{2-}$ this gives the following MO scheme:

$$\begin{align*}
&\pi^* \\
&\pi^\text{\text{non}} \\
&\pi^b \\
&\pi_1 \\
&\pi_2 \\
&\pi_3 \\
&\pi_4
\end{align*}$$

Like benzene, the system has six electrons, but only the pair in the bonding $\pi$ MO contributes to bonding. The two pairs in the non-bonding $\pi^\text{\text{non}}$ levels contribute nothing to bond stability. The one pair in $\pi^b$ contributes a total bond order of $\frac{1}{4}$ over four C–C linkages; i.e., $\frac{1}{4}$ to each C–C bond. With the single bond from $\sigma$ overlap, each C–C bond has a net bond order of $\frac{3}{4}$. This is significantly less than the $1\frac{1}{2}$ bond order in $C_6H_6$ and accounts for the lower stability of $C_4H_4^{2-}$.

6. Using VSEPR theory, indicate the domain geometry and molecular shape for each of the following, and sketch the shape. Indicate any angles that are expected to deviate from ideal electron-domain values (90°, 109.5°, 120°, 180°).

$\text{H}_2\text{Se}, \text{[BH}_4\text{]}, \text{SF}_4, \text{[H}_3\text{O}]^+, \text{[I}_3\text{]}^-, \text{[I}_3\text{]}^+, \text{[SbF}_5\text{]}^{2-}, \text{SO}_3, \text{SO}_3^{2-}, \text{SF}_3^+$.

$\text{H}_2\text{Se}$ domain geometry: tetrahedral shape: bent
\[\angle \text{H–Se–H} < 109.5^\circ (90.6^\circ)\]

$$\begin{array}{c}
\text{S} \\
\text{H} \quad \text{H}
\end{array}$$
BH$_4^-$

- Domain geometry: tetrahedral
- Shape: tetrahedral
- $\angle$H–B–H = 109.5° (no deviation)

\[
\begin{array}{c}
\text{H} \\
\text{B} \\
\text{H} \\
\text{H}
\end{array}
\]

SF$_4$

- Domain geometry: trigonal bipyramid
- Shape: disphenoid ("see-saw")
- $\angle$F$_{ax}$–S–F$_{ax}$ < 180° (173.1°), $\angle$F$_{eq}$–S–F$_{eq}$ < 120° (101.6°)

\[
\begin{array}{c}
\text{F} \\
\text{S} \\
\text{F}
\end{array}
\]

H$_3$O$^+$

- Domain geometry: tetrahedral
- Shape: trigonal pyramid
- $\angle$H–O–H < 109.5°

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

I$_3^-$

- Domain geometry: trigonal bipyramid
- Shape: linear
- $\angle$I–I–I = 180° (no deviation)

\[
\begin{array}{c}
\text{I} \\
\text{I}
\end{array}
\]
I$_3^+$  domain geometry: tetrahedral  
shape: bent  
$\angle$I–I–I $< 109.5^\circ$ (May actually be $>109.5^\circ$ due to lack of polarization of central I and large size of ligand I.)

\[
\begin{array}{c}
\hat{\text{I}} \\
\end{array}
\]

SbF$_5^{2-}$  domain geometry: octahedral  
shape: square pyramid  
$\angle$F$_{\text{basal}}$–Sb–F$_{\text{axial}}$ $< 90^\circ$

\[
\begin{array}{c}
\hat{\text{Sb}} \\
\end{array}
\]

SO$_3$  domain geometry: trigonal planar  
shape: trigonal planar  
$\angle$O–S–O $= 120^\circ$ (no deviation)

\[
\begin{array}{c}
\hat{\text{S}} \\
\end{array}
\]

SO$_3^{2-}$  domain geometry: tetrahedral  
shape: trigonal pyramid  
$\angle$O–S–O $< 109.5^\circ$

\[
\begin{array}{c}
\hat{\text{S}} \\
\end{array}
\]

SF$_3^+$  domain geometry: tetrahedral  
shape: trigonal pyramid  
$\angle$F–S–F $< 109.5^\circ$

\[
\begin{array}{c}
\hat{\text{S}} \\
\end{array}
\]